

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C25D 11/36	A1	(11) International Publication Number: WO 91/19836 (43) International Publication Date: 26 December 1991 (26.12.91)
(21) International Application Number: PCT/US91/03704 (22) International Filing Date: 28 May 1991 (28.05.91) (30) Priority data: 2/141647 1 June 1990 (01.06.90) JP (71) Applicant (for all designated States except US): HENKEL CORPORATION [US/US]; 300 Brookside Avenue, Am- bler, PA 19002 (US). (72) Inventors; and (75) Inventors/Applicants (for US only) : IMAI, Yasuo [JP/JP]; 5-101, Ohkurayama HAIMU, 891-2, Mamedo-cho, Koh- hoku-ku, Yokohama-shi, Kanagawa-ken (JP). HETSU- GI, Koji [JP/JP]; 16-62-405, Sodegahama, Hiratsuka-shi, Kanagawa-ken (JP). KOJIMA, Ryuji [JP/JP]; 2-34-9, Hongo, Bunkyo-ku, Tokyo (JP). NOZAWA, Hironobu [JP/JP]; 1-2, Aza Denjiyama, Narumi-cho, Midori-ku, Nagoya-shi, Aichi-ken (JP).		(74) Agent: WISDOM, Norvell, E., Jr.; Henkel Corporation, 140 Germantown Pike, Suite 150, Plymouth Meeting, PA 19462 (US). (81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European pa- tent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (Euro- pean patent), IT (European patent), LU (European pa- tent), NL (European patent), SE (European patent), US. Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: METHOD FOR TREATING THE SURFACE OF STEEL (57) Abstract A high quality lubricating coating can be provided on iron, carbon steel, and other low alloy steel workpieces before cold working them by electrolysis at a current density of 2 - 20 A/dm ² for 1 - 30 seconds, with the workpiece as cathode, in an aqueous acidic electrolytic bath containing as its essential constituents water, free acid, 3 to 20 g/L of zinc ions, 3 to 20 g/L of phosphate ions, 3 to 40 g/L of nitrate ions, and substantially no complexing agents for zinc ions, the acidic electrolytic bath also having a zinc ions to phosphate ions weight ratio in the range from 0.7 to 1.4 and a nitrate ions to phosphate ions weight ratio in the range from 0.7 to 2.6.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LI	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
DE	Germany	MC	Monaco	US	United States of America
DK	Denmark				

METHOD FOR TREATING THE SURFACE OF STEEL**TECHNICAL FIELD**

The present invention relates to a novel surface treatment method which may be applied in-line at high speeds to form a highly adherent, uniform, fine, and dense phosphate film on the surface of iron and steel, particularly carbon steel wire rod. More particularly, the present invention relates to a novel surface-treatment method which is an excellent lubrication treatment for the in-line drawing of carbon steel wire rod and which can also be effectively applied to low alloy steels.

BACKGROUND ART

An example of an in-line method for the formation of phosphate film on the surface of steel wire rod consists of scale removal from the wire rod surface by shot blasting, cleaning the surface, and, finally, forming a phosphate film by spray or immersion contact between a suitable liquid phosphating composition and the cleaned surface. If it is desired to increase the speed of such a line, the following possibilities would appear within the skill of those of ordinary skill in the art: (1) In anticipation of a need for higher speed operations, the equipment installed will have already been designed to accommodate variations in the length of the treatment zone; or (2) The reactivity can be improved by increasing the concentration of the conversion treatment bath, increasing the concentration of the film forming accelerator, and/or raising the temperature.

However, tactic (1) requires room for equipment space in order to obtain long treatment zone lengths and is associated with increased equipment costs, and its implementation may be restricted by existing equipment. In the case of tactic (2), in addition to increased treatment bath costs, sludge formation in the treatment bath is increased, and increased effort is required for bath management.

Additionally, several inventions have appeared which teach electrolysis in a phosphate treatment bath as a means for improving the phosphate film or for the formation of

such a film on the surface of corrosion resistant alloy steel. Although these inventions are not directed to wire rod, they are cited as art which is relevant to the present invention and are briefly summarized below.

- 5 (a) British Patent Number 1,041,761 (1966) teaches that, after formation of a zinc phosphate film, cathodic electrolysis is conducted in the same treatment bath in order to close the pinholes in the crystalline film with precipitated zinc particles and thus improve the film's corrosion resistance.
- 10 (b) Japanese Patent Number 46-15408 [15,408/71] teaches that an improvement in the conversion film's corrosion resistance, can be obtained by a process as follows: a steel article is immersed in a zinc phosphate bath; it is first subjected to anodic electrolysis in order electrically to accelerate elution of iron from the article; electrolysis is then halted; and phosphate film formation is conducted in the same bath.
- 15 (c) Japanese Patent Number 54-29979 [29,979/79] teaches that, in order to form a zinc phosphate film on the surface of corrosion-resistant alloy steel, zinc is deposited on the surface by cathodic electrolysis in a chelate compound-containing zinc phosphate treatment bath, electrolysis is halted, and a zinc phosphate film is formed on the plated surface in the same treatment bath.
- 20 (d) Japanese Patent Number 57-47277 [47,277/82] teaches that a composite film of zinc plate and zinc phosphate is formed by electrolysis with the workpiece being treated as cathode in a bath made up by adding a chloride (KCl or NaCl) to an aqueous solution of primary zinc phosphate.
- 25 (e) Japanese Patent Number 60-46197 [46,197/85] teaches that, in order to improve the corrosion resistance, a treatment workpiece already carrying a phosphate film is brought into contact with a zinc phosphate treatment bath and subjected to alternating current or di-
- 30
- 35

rect current electrolysis.

When this art of improving zinc phosphate films by electrolytic treatment was examined for its applicability as an in-line treatment, it was found that (a) involves film formation followed by electrolysis, (b) involves electrolysis followed by film formation, and (e) involves film formation followed by electrolysis. Thus, all of these involve a two-step treatment, which substantially compromises their utility as high speed treatments. Furthermore, (c) teaches the formation of a zinc phosphate film on corrosion resistant alloy, for example, stainless steel, and thus has a different object from the major object of the present invention. Finally, (d) concerns the formation of a composite film of zinc phosphate and metallic zinc particles. Such a film is only weakly adherent to the base metal and is also somewhat brittle, and these properties severely impair its utility as a base coat for lubrication. Thus, there is little possibility that any of the preceding inventions can be obviously applied to the major object of the present invention.

DESCRIPTION OF THE INVENTION

Problem to Be Solved by the Invention

The present invention has as its major object the provision of a novel method for the in-line, high speed formation of a strongly adherent, uniform, dense, and finely crystalline zinc phosphate film on the surface of carbon steel wire rod. The method is also applicable to other types of carbon steel and low alloy steel bodies that need to be lubricated prior to drawing or other cold working operations.

Summary of the Invention

A major embodiment of the present invention is a method in which a phosphate film is formed on the surface of an iron, carbon steel, or other low alloy steel workpiece by subjecting the workpiece cathodic electrolysis in an acidic electrolytic bath whose essential components are water, free acidity, and 3 to 20 grams per liter (hereinafter

"g/L") of zinc ions, 3 to 20 g/L of phosphate ions, and 3 to 40 g/L of nitrate ion; in which the zinc ion to phosphate ion weight ratio is in the range from 0.7 to 1.4 and the nitrate ion to phosphate ion weight ratio is in the range from 0.7 to 2.6; and which does not contain substantial amounts of any complexing agent for zinc ions.

These conditions make possible the high speed formation of a strongly adherent, uniform, finely crystalline, and dense phosphate film on the surface of workpieces as noted, particularly carbon-steel wire rod.

Details of Preferred Embodiments of the Invention

The appropriate ranges for the zinc (Zn^{+2}) ions, phosphate ions (PO_4^{-3}), and nitrate ions (NO_3^-) in the electrolytic bath are, respectively, 3 to 20 g/L, 3 to 20 g/L, and 3 to 40 g/L. In determining these concentrations, phosphoric acid and any anions produced by its ionization are considered as their stoichiometric equivalents of phosphate ions. When one, two, or all of these components falls below these lower limits, the formation of a film which achieves the object of the present invention becomes almost impossible. On the other hand, exceeding the given upper limits not only entails high economic costs, but it becomes problematic to obtain a highly adherent film as the concentration increases. Even more preferred ranges are 5 to 10 g/L for the zinc ions, 5 to 10 g/L for the phosphate ions, and 5 to 20 g/L for the nitrate ions.

In addition, while remaining within these limits on the concentration ranges for each component, the zinc ions to phosphate ions weight ratio (hereinafter "X") should be maintained in the range from 0.7 to 1.4 and the nitrate ions to phosphate ions weight ratio (hereinafter "Y") should be maintained within the range from 0.7 to 2.6.

With regard to the zinc ion/phosphate ion ratio, when X falls below 0.7, zinc codeposition can easily occur and a high quality film can not then be obtained. Moreover, the adhesion between the film and workpiece is poor at such values of X. Values of X in excess of 1.4 adversely affect

the costs of bath management.

With regard to the nitrate ion/phosphate ion ratio, values of Y less than 0.7 make it difficult to maintain the bath balance. Values of Y in excess of 2.6 retard the development of the necessary film weights due to nitric acid auto-oxidation.

Thus, as explained above, values for X or Y outside the ranges claimed for the present invention are associated with poor economics and problematic bath management, or impede the formation of a dense, finely crystalline, highly adherent film, and thus do not afford generally satisfactory results as a lubricant for plastic working (cold working) processes.

In order to inhibit or suppress the formation of a composite zinc phosphate film arising from the deposition of zinc particles or zinc plating, the electrolytic bath used by the present invention must not contain substantial amounts of any complexing agent for zinc. Such complexing agents include all halide ions except fluoride; oxygen and sulfur containing organic compounds; nitriles; cyanide and sulfide ions; and ammonia, phosphine, and arsine and amines and organo phosphines and arsines. Phosphoric acid and nitric acid and any anions produced by ionization of either of them are not considered complexing agents for zinc ions for the description of this invention.

The electrolytic bath under consideration may contain other heavy metal ions than zinc, e.g., nickel, manganese, magnesium, calcium, and the like, for codeposition as their phosphates in the conversion coating formed by the invention.

As already noted briefly above, it is preferable that little or no metallic inclusions be codeposited with the phosphate conversion film formed by a process according to this invention. In particular, the weight percentage of elemental metals such as zinc in the film is, with increasing preference, not greater than 10, 2, 0.5, 0.08, or 0.001 percent; and, independently, the areal density of me-

tallic elements in the coating formed is, with increasing preference, not more than 1, 0.3, 0.04, or 0.002 grams per square meter (hereinafter "g/m²") of the workpiece surface.

Preferred process conditions include surface cleaning the workpiece, preferably by shot blasting, before electrolysis; the electrolytic bath being maintained at 20 to 90 ° C; an anode of carbon plate; an inter electrode distance in the range from 2 to 30 cm and more preferably from 3 to 10 cm; a current density in the range from 2 to 20 amps per square decimeter (hereinafter "A/dm²") of workpiece surface, more preferably from 5 to 10 A/dm². While the electrolysis time will vary with the current density, a strongly adherent, uniform, dense, and finely crystalline phosphate film with a preferred coating weight of from 3 to 20 g/m² can normally be formed in 1 to 30 seconds, so that a time within this range is preferred.

Because the free phosphoric acid concentration in the electrolytic bath undergoes transient increases during electrolysis, it is preferred during prolonged operation of a process according to this invention to maintain the acid concentration within the appropriate range through the addition at suitable times of a dilute aqueous solution of sodium or potassium hydroxide or carbonate. Also, it is usually necessary during prolonged operation to maintain the concentration of phosphate ions in the electrolytic bath within the appropriate range through the supply at suitable times of concentrated phosphate solution which has been suitably adjusted for the electrolytic bath under consideration.

The practice of the method of the present invention will be described below using Examples 1 - 5 (working examples according to the invention) and Comparison Examples 1 - 6.

Examples

General Conditions

Testing was carried out on 3 millimeter (hereinafter "mm") diameter Type S43C steel wire. Pretreatment con-

sisted of the following: degreasing with a solution in water of FINE CLEANER™ 4360 (from Nihon Parkerizing Company, Ltd.) at 20 g/L and 55 ° C for 1 minute; then a water wash with tap water; then an acid wash for 3 minutes at ambient temperature with 10% aqueous hydrochloric acid followed by a water wash with tap water.

Electrolytic conversion was conducted as follows: bath composition as described in Table 1, maintained at 55 ° C; electrolysis time = 10 seconds; current density = 7 A/dm²; cathode = wire rod workpiece in the electrolytic bath; inter-electrode distance = 10 cm; carbon plate anodes placed at two locations. These electrolytic conversion conditions are designated as standard, and any deviations therefrom will be explicitly specified below. The workpiece was then washed with tap water and dried in a hot air current. The film weight was subsequently measured by immersion in 3 % aqueous chromic acid at 80° C for 15 minutes to strip off the film and determination of the weight difference caused by stripping. The presence of codeposited metallic zinc was evaluated by X-ray diffraction.

Lubrication testing was conducted as described below. The test conditions were designed with the recognition that in normal use, drawing is performed through a plurality of dies in succession. Therefore, the lubricity of the coating remaining on a test wire after drawing through one die is representative of the practical lubricating effect to be expected from a particular lubricating coating.

Details of the lubrication testing were as follows: The 3.0 mm diameter wire rod was drawn to 2.4 mm diameter on a drawing machine, with the wire rod being dusted with calcium stearate immediately ahead of the die. The lubrication quality of the film remaining on the wire rod with reduced cross section after drawing was subsequently evaluated using a Bowden tester under the following conditions: test instrument was Model EFM-4 from Orientek Corporation, ambient temperature, load = 5 kg, slider = 5 mm diameter SUJ2 cylinder, sliding distance = 20 mm, sliding velocity

= 6 mm/minute. The apparatus measures the frictional force required to move the slider along the length of the wire rod, and the coefficient of friction μ is defined as the ratio of this frictional force to the load on the slider. Initial values of μ are well below 0.25, but continued operation of the apparatus eventually wears through or otherwise damages the lubricating coating, so that the measured values of μ rise. The number of sliding strokes to reach a friction coefficient of 0.25 was determined and was designated as the number to seizure.

Examples 1 to 5

Examples 1, 2, 3, 4, and 5 concerned testing as described above on, respectively, film-forming compositions A, B, C, D, and E set forth in Table 1, and Table 1 also reports the results therefrom (film weight, zinc metal deposition, number of sliding strokes).

Comparison Examples 1 to 5

Comparison Examples 1, 2, 3, 4, and 5 concerned testing as described above on, respectively, film-forming agents F, G, H, I, and J as set forth in Table 1, and Table 1 also reports the results therefrom (film weight, zinc metal deposition, number of sliding strokes). In addition, zinc deposition in the bath was observed for treatment bath compositions G and H, and the bath balance was thus disrupted.

Comparison Example 6

This concerned the formation of a conversion film using a bath composition of 90 g/L PARBONDTM 181X (zinc phosphate system conversion coating agent commercially available from Nihon Parkerizing Co., Ltd.) and 0.34 g/L AC-131TM (also commercially available from Nihon Parkerizing Co., Ltd.) as accelerator at a temperature of 80° C with an immersion time of 15 minutes. The other conditions were the same as in the test method described above, and the test results from this Comparison Example are also reported in Table 1.

Table 1. Bath compositions

	A	B	C	D	E
Zn g/L	8	10	10	8	5
PO ₄ g/L	10	8	10	10	6
NO ₃ g/L	10	14	15	26	7
Zn/PO ₄	0.8	1.25	1.0	0.8	0.8
NO ₃ /PO ₄	1.0	1.75	1.5	2.6	1.16
film weight	8.3	9.5	9.6	7.2	7.3
deposition of metallic zinc	none	none	none	none	none
number of sliding strokes (see note 1)	298	304	283	282	321

(Table 1 is continued on the next page)

Note 1: This number of sliding strokes equals the seizure starting point, i. e., the point at which the friction coefficient reached 0.25 or more

Table 1. Bath compositions (Continued from the previous page)

	F	G	H	I	J	K
Zn g/L	5	10	10	5	2	note 2
PO ₄ g/L	10	6	10	10	2	
NO ₃ g/L	10	10	5	5	3	
Zn/PO ₄	0.5	1.67	1.0	0.5	1.0	
NO ₃ /PO ₄	1.0	1.65	0.5	0.5	1.5	
film weight	3.2	4.2	3.8	5.2	1.8	6.7
deposition of metallic zinc	deposition	none	none	deposition	none	none
number of sliding strokes (see note 1)	127	98	41	93	53	264

Note 1: This number of sliding strokes equals the seizure starting point, i. e., the point at which the friction coefficient reached 0.25 or more

Note 2: Conversion film-forming bath of Comparison Example 6

The obtained results show that there is no significant deposition of metallic zinc with the present invention, and that the present invention affords a phosphate film which is in no way inferior to phosphate films used heretofore.

- 5 In addition, as demonstrated by the test results from the comparison examples, when the ranges specified for the present invention were not met, the number of sliding strokes was smaller than even in the prior art, and zinc deposition was observed.

CLAIMS

1. A method for forming a zinc phosphate containing conversion coating that is substantially free from elemental metal on the surface of a workpiece selected from the group of iron, carbon steel, and low alloy steels, characterized in that the workpiece is subjected to cathodic electrolysis in an acidic electrolytic bath whose essential components are water, free acid, 3 to 20 g/L of zinc ions, 3 to 20 g/L of phosphate ions, and 3 to 40 g/L of nitrate ions, said acidic electrolytic bath optionally also including cations of heavy metals other than zinc, said acidic electrolytic bath being further characterized in that the zinc ions to phosphate ions weight ratio is in the range from 0.7 to 1.4, the nitrate ions to phosphate ions weight ratio is in the range from 0.7 to 2.6, and that it contains substantially no complexing agents for zinc ions.
2. A method according to claim 1, characterized in that the acidic electrolytic bath contains from 5 to 10 g/L of zinc ions, from 5 to 10 g/L of the phosphate ions, and from 5 to 20 g/L of the nitrate ions.
3. A method according to claim 2, wherein the temperature of the electrolytic bath is maintained within the range from 20 to 90 ° C while the bath is in contact with the workpiece.
4. A method according to claim 1, wherein the temperature of the electrolytic bath is maintained within the range from 20 to 90 ° C while the bath is in contact with the workpiece.
5. A method according to claim 4, wherein the cathodic current density on the workpiece is in the range from 2 to 20, or preferably from 5 to 10, A/dm².
6. A method according to claim 3, wherein the cathodic current density on the workpiece is in the range from 2 to 20, or preferably from 5 to 10, A/dm².

7. A method according to claim 2, where in the cathodic current density on the workpiece is in the range from 2 to 20, or preferably from 5 to 10, A/dm².
- 5 8. A method according to claim 1, wherein the cathodic current density on the workpiece is in the range from 2 to 20, or preferably from 5 to 10, A/dm².
9. A method according to claim 8, wherein the time of electrolysis is chosen so as to produce a coating weight in the range from 3 to 20 g/m².
- 10 10. A method according to claim 7, wherein the time of electrolysis is chosen so as to produce a coating weight in the range from 3 to 20 g/m².
11. A method according to claim 6, wherein the time of electrolysis is chosen so as to produce a coating weight in the range from 3 to 20 g/m².
- 15 12. A method according to claim 5, wherein the time of electrolysis is chosen so as to produce a coating weight in the range from 3 to 20 g/m².
13. A method according to claim 4, wherein the time of electrolysis is chosen so as to produce a coating weight in the range from 3 to 20 g/m².
- 20 14. A method according to claim 3, wherein the time of electrolysis is chosen so as to produce a coating weight in the range from 3 to 20 g/m².
- 25 15. A method according to claim 2, wherein the time of electrolysis is chosen so as to produce a coating weight in the range from 3 to 20 g/m².
16. A method according to claim 1, wherein the time of electrolysis is chosen so as to produce a coating weight in the range from 3 to 20 g/m².
- 30 17. A method according to any one of claims 1 - 16, wherein the workpiece is carbon steel wire rod.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 91/03704

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.C1.5 C 25 D 11/36		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.C1.5	C 25 D 11/36	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	EP,A,0288853 (NIHON PARKERIZING CO.) 2 November 1988 ---	
A	DE,C, 746271 (METALLGESELLSCHAFT AG) 17 June 1944 -----	
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁰ Special categories of cited documents : ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
26-09-1991		19 NOV 1991
International Searching Authority		Signature of Authorized Officer
EUROPEAN PATENT OFFICE		Mme N. KUIPER

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9103704
SA 48645

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 21/10/91
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0288853	02-11-88	JP-A- 63262500	28-10-88
		DE-A- 3812692	24-11-88
		US-A- 4874480	17-10-89
<hr/>			
DE-C- 746271		None	
<hr/>			